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(54) Oral sensory perception-affecting compositions containing dimethyl sulfoxide

(57) Described are oral sensory perception-affecting compositions containing dimethyl sulfoxide, complexes thereof and salts thereof, specifically:

- (i) dimethyl sulfoxide; and
- (ii) a second compound or group of compounds:

- (a) containing at least one menthly moiety; and/or
- (b) containing at least one vanillyl moiety; and/or
- (c) containing at least one carboxam-

ide moiety

when the weight ratio of "second compound(s)": dimethyl sulfoxide, is in the range of from about 1,000:1 down to about 3:10 and food grade acceptable salts thereof. Also described are oral sensory perception-affecting (e.g., "coolant")-impacting consumable articles (e.g., mouthwashes and the like) comprising a consumable article base and at least one of the aforementioned oral sensory perception-affecting compositions. Also described are complexes of (i) dimethyl sulfoxide and (ii) at least one of the aforementioned second compounds or group(s) of compounds.

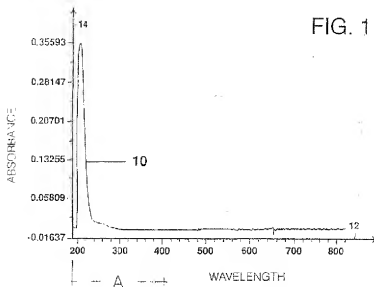


FIG. 1

## Description

[0001] Our invention relates to oral sensory perception-affecting compositions containing dimethyl sulfoxide, complexes thereof and salts thereof, specifically comprising (i) dimethyl sulfoxide and (ii) a second compound or group of compounds:

- (a) containing at least one menthyl moiety; and/or
- (b) containing at least one vanillyl moiety; and/or
- (c) containing at least one carboxamide moiety.

The term "oral sensory perception-affecting compositions" is intended to cover "coolant compositions" as well as "heat compositions."

[0002] Compositions containing compounds producing a cooling sensation, specifically hydroxy methyl or hydroxy ethyl derivatives of paramenthanes are disclosed in U.S. Letters Patent No. 4,029,759. Such compositions are disclosed to be useful, for example, for spearmint flavor used in toothpastes, as well as other ingestible materials such as margarine and the like. Breath freshening edible compositions of menthol and a carboxamide are disclosed in U.S. Letters Patent No. 5,009,893. "Hot, tingling, burning, numbing" causing sensations by use of 4-(1-menthoxyethyl)-2-phenyl-1,3-dioxolane or a derivative thereof is disclosed in U.S. Letters Patent No. 5,545,424 issued on August 13, 1996. Combinations of coolant compositions comprising a ketal and a secondary coolant which may be menthol are disclosed in PCT Application No. 93/23005 published on November 25, 1993. Production of chewing gum containing controlled release acyclic carboxamides as cooling agents are disclosed in PCT Application No. 99/13870 published on March 25, 1999. Chewing gum production using modified, physiological cooling agents, to wit: menthol, menthone and a carboxamide or a ketal or a diol or a succinate or mixtures of same, are disclosed in PCT Application No. 99/13734 published on March 25, 1999.

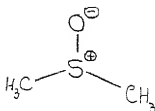
[0003] However, there exists an ongoing need to provide enhancement of such "hot" sensations or such "cooling" sensations in various edible compositions, including beverages, toothpastes, throat lozenges, mouthwashes, dental floss, chewing gums, edible films such as breath freshener films and chewable pharmaceutical products, particularly wherein such "enhancement" raises the level of the "hot" or "cooling" sensation on ingestion of the edible composition, on a scale of 0-10, from about 2 up to about 10. The provision of such enhancement properties has heretofore been unknown and not implied in any prior art. Accordingly, nothing in the prior art sets forth the use of combinations of dimethyl sulfoxide with compounds containing at least one menthyl moiety, compounds containing at least one vanillyl moiety and/or compounds containing at least one carboxamide moiety in order to enhance oral sensory perception, including "hot" sensations and "cool" sensations.

[0004] Indeed, the use of dimethyl sulfoxide in foodstuffs and the presence of dimethyl sulfoxide in foodstuffs is well known. Thus, dimethyl sulfoxide is set forth in the TNC Nutrition and Food Research Institute's *Volatile Compounds in Food: Qualitative and Quantitative Data*, Seventh Edition 1996 (Editors: L.M. Nijssen, et al.) at page 8 under CAS No. 67/68/5. Dimethyl sulfoxide is also on the GRAS list as published in *GRAS Flavoring Substances 18*, the 18th publication by the Flavor and Extract Manufacturers' Association's Expert Panel on recent progress in the consideration of the flavoring ingredients generally recognized as safe for use in food (reference: *Cooked Food Technology*, September 1998, Volume 52, No. 9 (GRAS No. 3875)) (also called "methyl sulfoxide," "DMSO" and "methyl sulfinyl methane.") Nothing in the prior art discloses the effect of dimethyl sulfoxide on other sensory affecting agents, particularly oral sensory perception-affecting compositions such as coolant compositions or "hot, burning, bitter" compositions.

## THE INVENTION

[0005] Our invention is directed to oral sensory perception-affecting compositions containing dimethyl sulfoxide, complexes thereof and salts thereof, specifically comprising:

- (i) dimethyl sulfoxide having the structure:



; and

(ii) a second compound or group of compounds:

- (a) containing at least one menthyl moiety; and/or
- (b) containing at least one vanillyl moiety; and/or
- (c) containing at least one carboxamide moiety,

wherein the weight ratio of "second compound(s)": dimethyl sulfoxide, is in the range of from about 1,000:1 down to about 3:1 and food grade acceptable salts thereof.

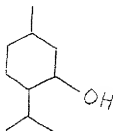
[0006] Our invention also covers oral sensory perception-affecting compositions (e.g., "coolants")-imparting consumable articles (e.g., beverages, toothpastes, throat lozenges, mouthwashes, dental floss, chewing gums, edible films and chewable pharmaceutical products). The sensory-affecting consumable articles having intensified and substantive sensory-affecting properties such as oral cooling properties and oral heating properties comprise (i) an ultimate product base and intimately admixed therewith (ii) a composition comprising (a) dimethyl sulfoxide and (b) a second compound or mixture of compounds selecting from the group consisting of compounds:

- (a) containing at least one menthyl moiety; and/or
- (b) containing at least one vanillyl moiety; and/or
- (c) containing at least one carboxamide moiety

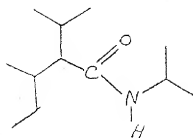
wherein the weight ratio of second compound or group of compounds: dimethyl sulfoxide, is in the range of from about 1,000:1 down to about 3:10 and food grade acceptable salts thereof, wherein the concentration of dimethyl sulfoxide based on the weight of ultimate product is from about 0.05 up to about 200 parts per million (ppm) and the concentration of second compound or group of compounds or mixture of compounds is from about 2 ppm up to about 10,000 ppm on a mixed basis.

[0007] Examples of the "second compound" to be admixed with the dimethyl sulfoxide forming the mixtures of our invention are as follows:

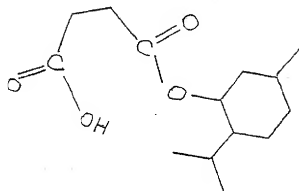
menthol having the structure:



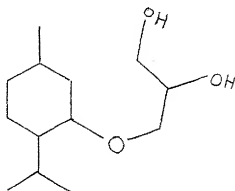
WS 23® (registered trademark of the Warner Lambert Company) having the structure:



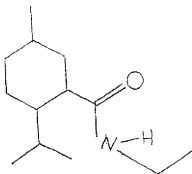
menthyl succinate having the structure:



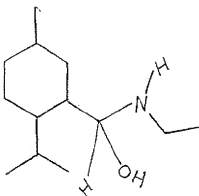
the monomenthyl ether of glycerin having the structure:



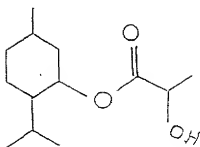
WS 3® (registered trademark of the Warner Lambert Company) having the structure:



the compound having the structure:



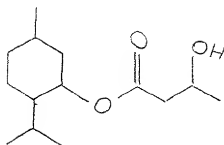
the compound having the structure:



the compound having the structure:

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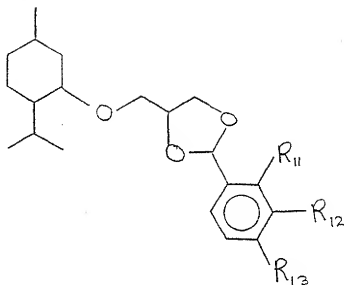
15 the compound having the structure:

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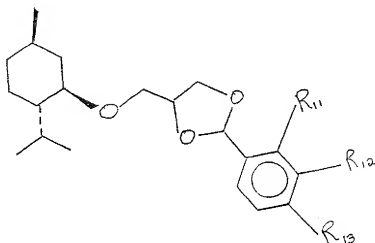
the compound having the structure:

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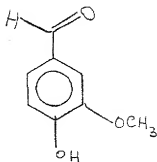
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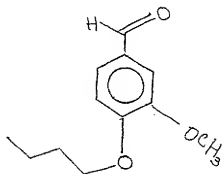
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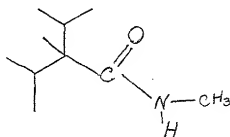
the compound having the structure:



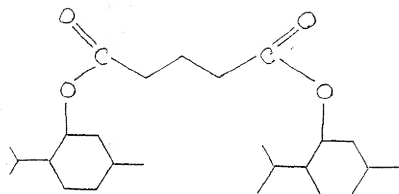
the compound having the structure:



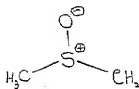
the compound having the structure :



and the compound having the structure :



[0008] When dimethyl sulfoxide having the structure:



is admixed with such "second compound(s)," the resulting mixture as stated, supra, has a highly intensified oral sensory perception effect, for example, a "highly intensified cooling effect" or a "highly intensified hot, burning effect." Such effects are highly desirable in the use of certain oral care products such as mouthwashes, toothpastes and the like as set forth, supra. Thus, the following Table I sets forth a comparison of a "control" which is a "second compound" taken alone vs. the mixture of dimethyl sulfoxide with the said "second compound":

TABLE I

"Second Compounds"	Second Compound (ppm)	Dimethyl Sulfoxide (DMSO) (ppm)	Effect of Mixture vs. Control -- Comparison on a Scale 0-10
Menthol	5	0.1	increase in perceived cooling - 8 vs. 1.6
Menthol	10	1	increase in perceived cooling - 9 vs. 1.3
Menthol	30	5	increase in perceived cooling - 9.5 vs. 1.1
Menthol	100	10	increase in perceived cooling - 8.7 vs. 2
Menthyl lactate	30	0.1	increase in perceived cooling - 8.4 vs. 1.7
Menthyl lactate	30	100	increase in perceived cooling - 8.2 vs. 2.1
Monomenthyl succinate	100	0.1	increase in perceived cooling - 9.1 vs. 3.8



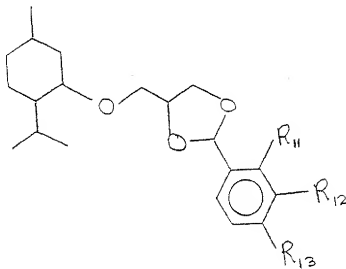
TABLE I (continued)

"Second Compounds"	Second Compound (ppm)	Dimethyl Sulfoxide (DMSO) (ppm)	Effect of Mixture vs. Control -- Comparison on a Scale 0-10
Monomethyl succinate	100	100	increase in perceived cooling - 8.7 vs. 2.5
50-50 (weight-weight) Mixture of mono- and dimethyl glutarates	100	0.1	increase in perceived cooling - 9.6 vs. 3.3
50-50 (weight-weight) Mixture of mono- and dimethyl glutarates	100	100	increase in perceived cooling - 9.4 vs. 3.2
WS 3® <sup>1</sup>	30	0.1	increase in perceived cooling - 9.3 vs. 1.5
WS 3® <sup>1</sup>	30	100	increase in perceived cooling - 9.0 vs. 1.6
WS 23® <sup>2</sup>	30	0.1	increase in perceived cooling - 9.6 vs. 2.4
WS 23® <sup>2</sup>	30	100	increase in perceived cooling - 9.2 vs. 2.2
TAKOOL® <sup>3</sup>	30	0.1	increase in perceived cooling - 8.6 vs. 2.8
TAKOOL® <sup>3</sup>	30	100	increase in perceived cooling - 8.2 vs. 2.6

Notes: <sup>1</sup> WS 3® is a registered trademark of the Warner Lambert Company;

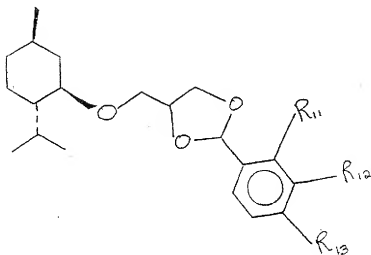
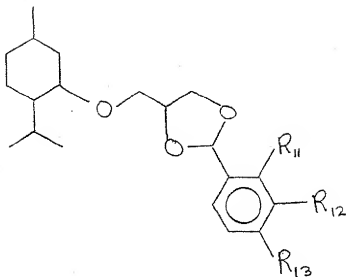
<sup>2</sup> WS 23® is a registered trademark of the Warner Lambert Company; and

<sup>3</sup> TAKOOL® is a registered trademark of Takasago International Corporation of Tokyo, Japan and has the structure:



wherein R<sub>11</sub>, R<sub>12</sub> and R<sub>13</sub> each represent hydrogen.

[0009] When the second compounds are defined according to the structures:



45  $R_{11}$ ,  $R_{12}$  and  $R_{13}$  each represents the same or different hydrogen, methyl, ethyl, n-propyl or isopropyl. Such compounds are set forth in U.S. Letters Patent No. 5,545,424, the specification for which is incorporated by reference herein.

[0010] The following Table I sets forth the effect in a screening base, in this case: silica toothpaste base containing 0.4% saccharin of various "second compounds" in admixture with dimethyl sulfoxide, as follows:

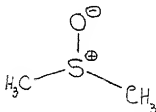
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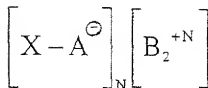
TABLE II

Use Level of 2 <sup>nd</sup> Compound ppm DMSO Observed Effect -- Scaled at 1-10				
Screening Base	2 <sup>nd</sup> Compound (Coolant)	Use Level of 2 <sup>nd</sup> Compound	ppm Dimethyl Sulfoxide (DMSO)	Observed Effect Scaled at 1-10 vs. 2 <sup>nd</sup> Compound Alone
Silica toothpaste base with 0.4% saccharin	Menthol	0.50%	1	increase in perceived cooling - 8.2 vs. 1.6
Silica toothpaste base with 0.4% saccharin	Monomenthyl succinate	100 ppm	0.1	increase in perceived cooling - 9.0 vs. 3.5
Silica toothpaste base with 0.4% saccharin	Monomenthyl succinate	100 ppm	1	increase in perceived cooling - 9.2 vs. 3.7
Silica toothpaste base with 0.4% saccharin	50-50 (Weight-weight) mono-and dimenthyl glutarates	100 ppm	0.1	increase in perceived cooling - 9.7 vs. 3.4
Silica toothpaste base with 0.4% saccharin	50-50 (Weight-weight) mono-and dimenthyl glutarates	100 ppm	1	increase in perceived cooling - 9.6 vs. 3.3
Silica toothpaste base with 0.4% saccharin	WS 3®	30 ppm	0.1	increase in perceived cooling - 9.1 vs. 1.7
Silica toothpaste base with 0.4% saccharin	WS 3®	30 ppm	1	increase in perceived cooling - 9.0 vs. 1.6
Silica toothpaste base with 0.4% saccharin	WS 23®	30 ppm	0.1	increase in perceived cooling 9.8 vs. 2.4
Silica toothpaste base with 0.4% saccharin	WS 23®	30 ppm	1	increase in perceived cooling 9.9 vs. 2.6

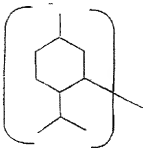
[0011] More specifically, our invention includes coolant compositions having intensified and substantive cooling properties, as well as heat sensation-imparting compositions having intensified and substantive heat-imparting properties, consisting essentially of a product produced by the step of admixing dimethyl sulfoxide having the structure:



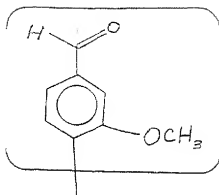
with at least one coolant or heat sensation-imparting compound having a formula selected from the group consisting of X-A-H; X-A-B<sub>1</sub>; and



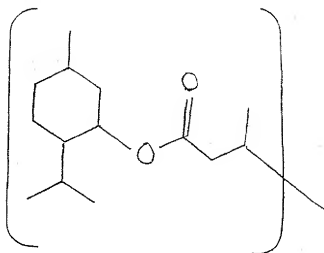
wherein the weight ratio of "coolant" or "heating" compound, dimethyl sulfoxide, is from 1,000:1 up to 3:10 and wherein X represents menthyl having the structure:



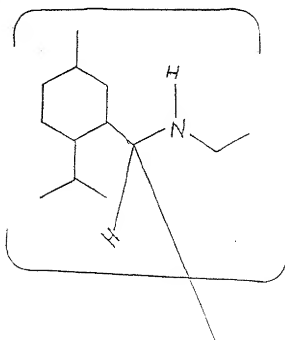
or vanillyl having the structure:



or a moiety having the structure:



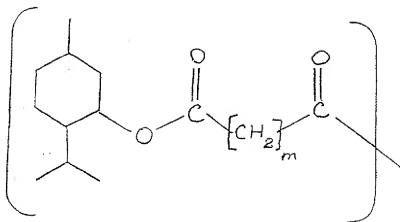
and a moiety having the structure:



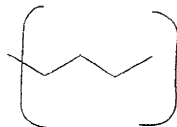
or menthoxy maleyl, succinyl, glutaryl or the like having the structure:

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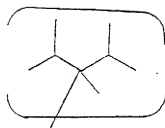
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wherein m is an integer of from 1 up to 4; or n-butyl having the structure:



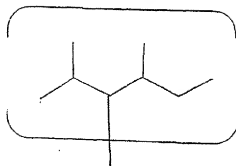
or 2,3,4-trimethyl-3-pentyl having the structure:



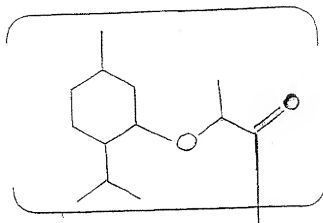
or 2,4-dimethyl-3-hexyl having the structure:

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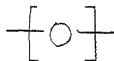
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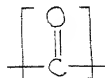
or menthoxy lactyl having the structure:



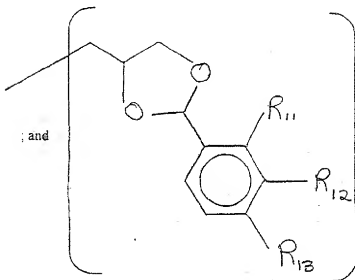
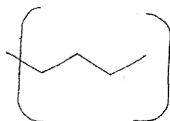
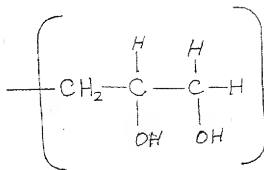
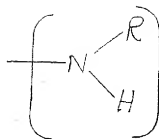
wherein A represents a divalent ether or alcohol linkage having the structure:



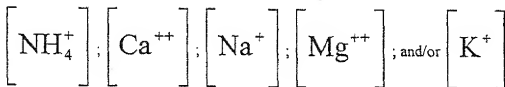
or a divalent carbonyl linkage having the structure:



wherein B<sub>1</sub> represents one of the moieties:



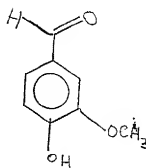
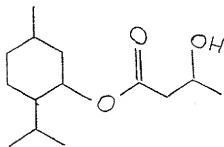
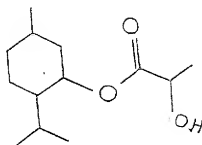
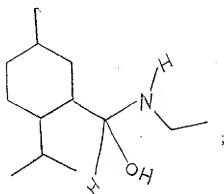
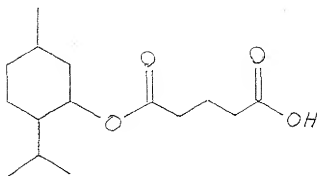
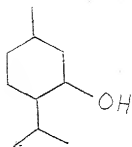
wherein  $\text{R}_{11}$ ,  $\text{R}_{12}$  and  $\text{R}_{13}$  are each the same or different and each represents hydrogen and  $\text{C}_1$ - $\text{C}_3$  lower alkyl, that is, methyl, ethyl, n-propyl or i-propyl; and wherein  $\text{B}_2$  represents one of the cations:

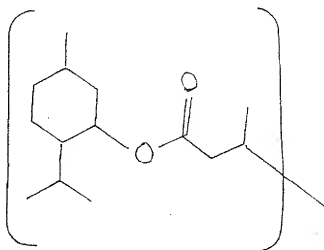
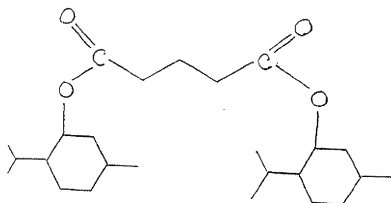


and wherein  $\text{N}$  represents an integer of 1 or 2.

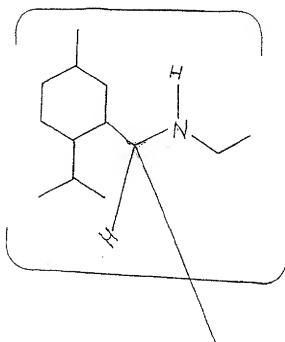
[0012] Examples of the compounds represented by the structure: X-A-H are as follows:



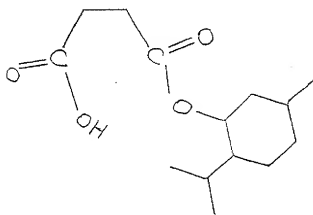




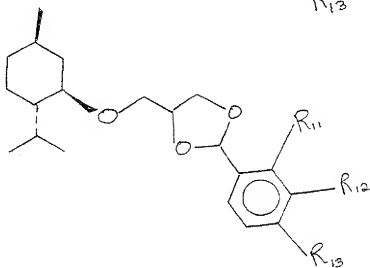
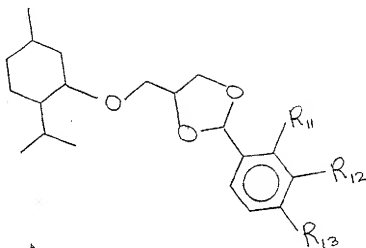
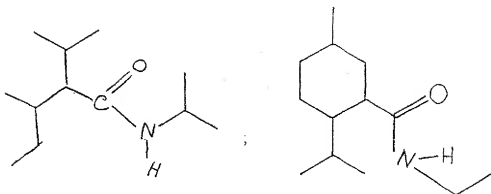
and



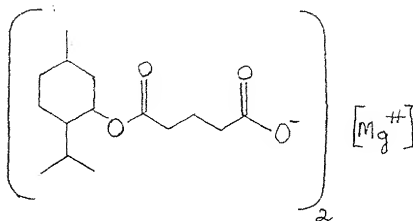
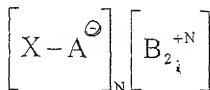
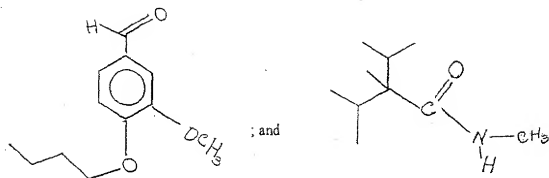
[0013] Another example of a compound represented by the structure: X-A-H is the compound having the structure:

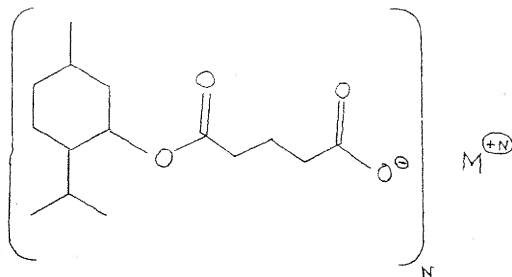


[0014] Examples of compounds represented by the structure: X-A-B<sub>1</sub> are as follows:

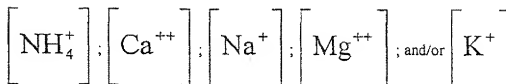


(wherein  $R_{11}$ ,  $R_{12}$  and  $R_{13}$  are the same or different and each represents hydrogen or  $C_1$ - $C_3$  lower alkyl);





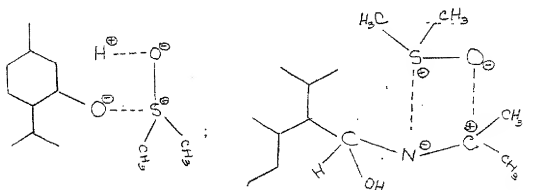
(wherein N is 1 or 2 and wherein M represents one of the cations:

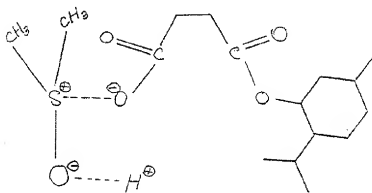
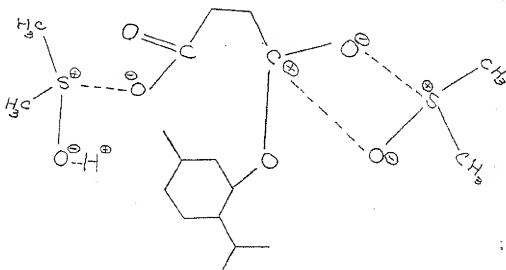
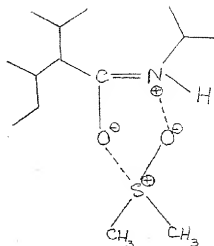
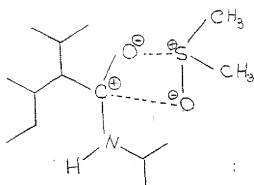


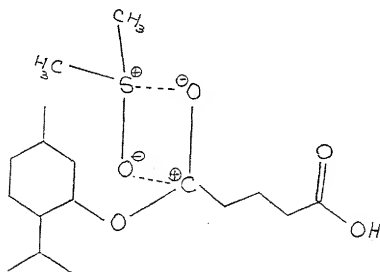
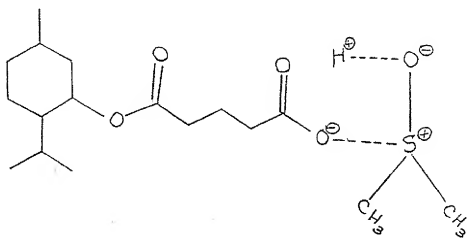
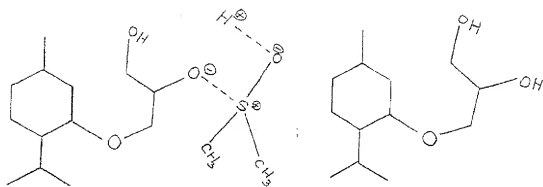
[0015] When the dimethyl sulfoxide is in admixture with one of the compounds represented by one of the structures: X-A-H; X-A-B<sub>1</sub>; and/or



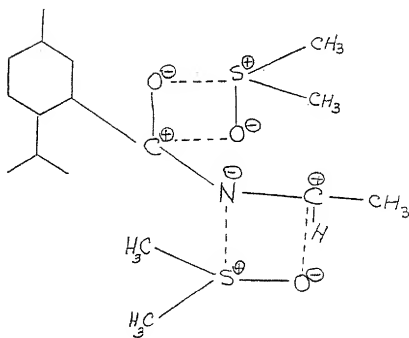
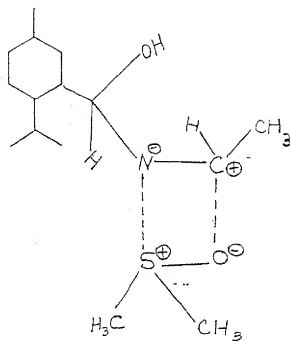
then complexes are formed exemplified by those having the following structures:

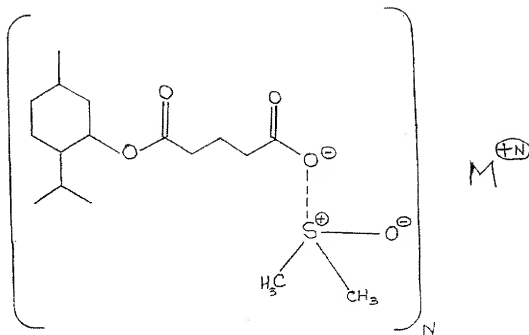
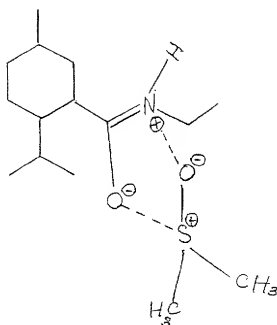












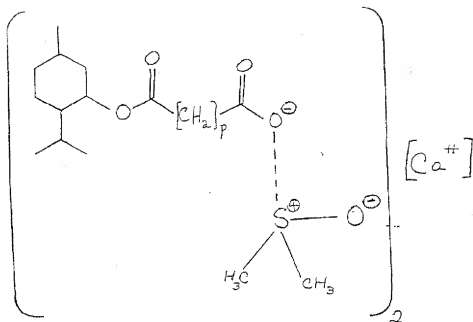
(wherein M is a cation as defined, supra; and N is an integer of 1 or 2);

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(wherein p is an integer of from 1 up to 3);

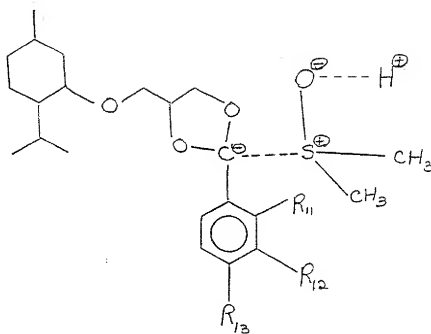
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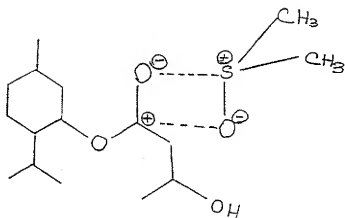
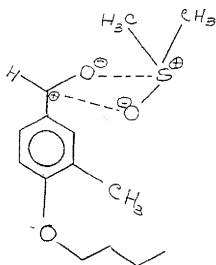
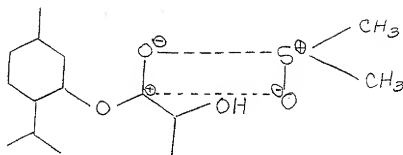
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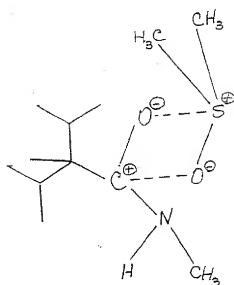
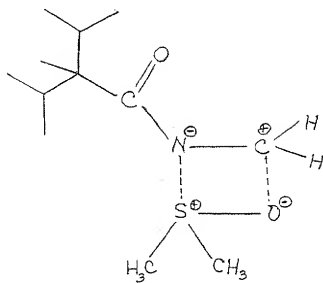
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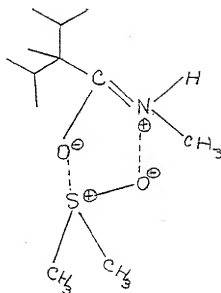
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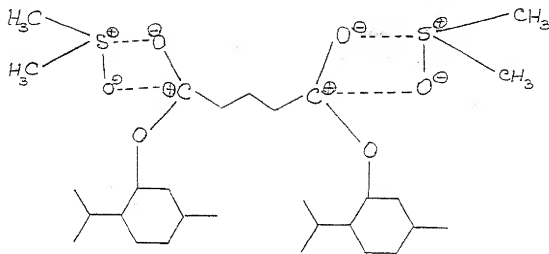
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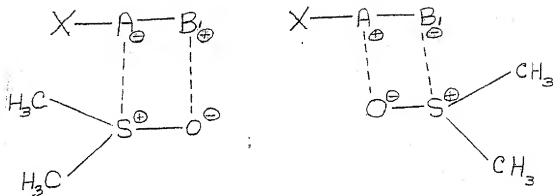




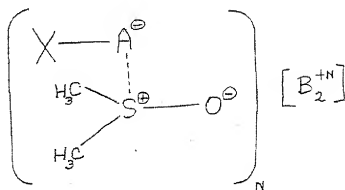
and



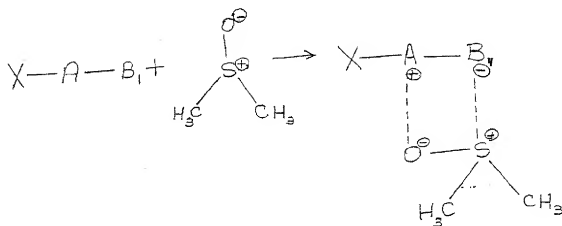
[0016] Such complexes are shown using the generic formulae:

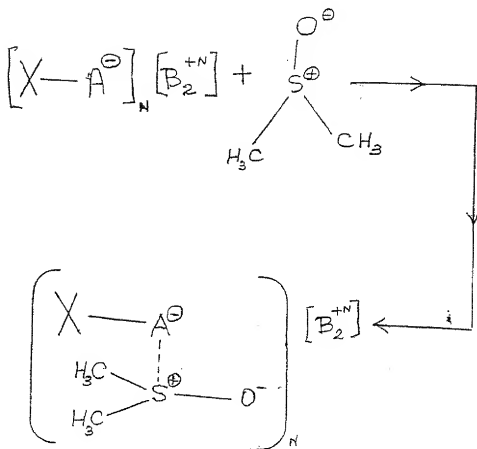


and



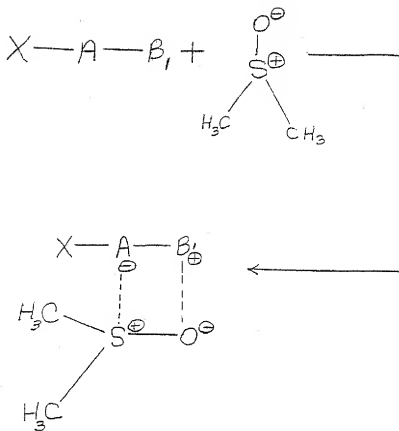
[0017] Generic reactions to form said complexes are as follows:



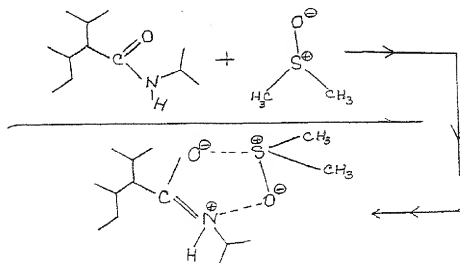


and

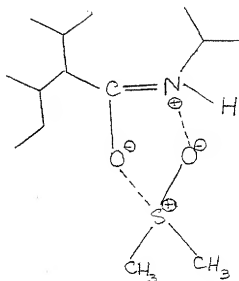




[0018] A specific reaction to form such a complex is set forth as follows:



whereby the complex having the structure:



is formed.

[0019] In each of the consumable articles produced according to our invention, that is, in the beverages, toothpastes, throat lozenges, mouthwashes, dental floss, chewing gums, edible films and chewable pharmaceutical products of our invention, the concentration of dimethyl sulfoxide (on a premixed basis) based on the weight of ultimate product is from about 0.05 up to about 200 ppm. In each of the consumable articles of our invention, the concentration of second compound, that is one of the compounds having one of the structures:  $X-A-H$ ;  $X-A-B_1$ ; and/or



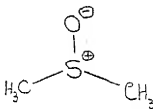
on a premixed basis, based on the weight of the ultimate product, is from about 2 up to about 10,000 ppm.

[0020] An example of a breath freshener film is one produced from pullulan and modified starches containing 5% actives as produced by the Warner Lambert Company. Another example is HERB LEAF® produced by the Ha-Bur-Fu K.K. Organization of Japan under the trademark HERB LEAF® (registered trademark of the Ha-Bur-Fu K.K. Organization), specifically described in Japanese Patent No. 1843452, the specification for which is incorporated by reference herein. Other examples of products wherein the compositions of our invention are useful are as follows:

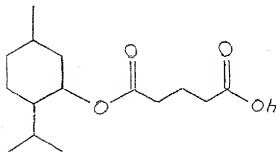
- (a) toothpaste as disclosed in Examples 6-10 of U.S. Letters Patent No. 4,029,759 issued on June 14, 1977, the specification for which is incorporated by reference herein;
- (b) chewing gum compositions as set forth in Example 1 at column 10 of U.S. Letters Patent No. 5,009,893 issued on April 23, 1991, the specification for which is incorporated by reference herein;
- (c) hard candy (formed into throat lozenges) as exemplified in Example 4 of U.S. Letters Patent No. 5,545,424 issued on August 13, 1996, the specification for which is incorporated by reference herein;
- (d) mouth rinse formulations as set forth in Examples 3 and 4 of PCT Application No. WO 93/23005 published on November 25, 1993, the specification for which is incorporated by reference herein;
- (e) sugarless gums as set forth in Examples 30-37 in Table 7 of PCT Application No. WO 99/13870 published on March 25, 1999, the specification for which is incorporated by reference herein; and
- (f) chewing gums as exemplified in Examples 6-10 in Table 3 of PCT Application No. WO 99/13734 published on March 25, 1999, the specification for which is incorporated by reference herein.

**BRIEF DESCRIPTION OF THE DRAWINGS**

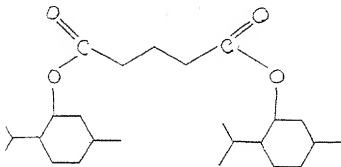
[0021] Figure 1 is an ultraviolet - visible spectrum for a 1:1 mixture of dimethyl sulfide having the structure:



:menthyl glutarates, a mixture of compounds having the structure:



and



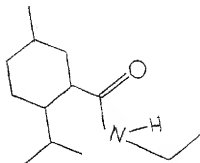
(solvent: methanol; concentration: 0.01%; wavelength range: 190-820 nm).

[0022] Figure 1A is an ultraviolet spectrum (only) for a 1:1 mixture of dimethyl sulfoxide:menthyl glutarates (conditions: methanol solvent at a concentration of 0.01%; wavelength range: 190-400 nm).

[0023] Figure 2 is an ultraviolet-visible spectrum for a 10:1 mixture of dimethyl sulfoxide:menthyl glutarates (conditions: methanol solvent at a 1% concentration; wavelength range: 190-820 nm).

[0024] Figure 2A is an ultraviolet (only) spectrum for a 10:1 mixture of dimethyl sulfoxide:menthyl glutarates mixture (conditions: methanol solvent at a 1% concentration; wavelength range: 190-400 nm).

[0025] Figure 3 is an ultraviolet-visible spectrum for a 1:1 mixture of dimethyl sulfoxide:WS 3® (registered trademark of the Warner Lambert Company) having the structure:



(conditions: methanol solvent at a concentration of 0.01%; wavelength range: 190-820 nm).

[0026] Figure 3A is an ultra violet spectrum (only) for a 1:1 mixture of dimethyl sulfoxide:WS 3® (conditions: methanol solvent at a concentration of 0.01%; wavelength range: 190-400 nm).

[0027] Figure 4 is an ultraviolet-visible spectrum (only) for a 10:1 mixture of dimethyl sulfoxide:WS 3® (conditions: methanol solvent at a concentration of 1.0%; wavelength range: 190-820 nm).

[0028] Figure 4A is an ultraviolet spectrum (only) for a 10:1 mixture of dimethyl sulfoxide:WS 3® (conditions: methanol solvent at a concentration of 1.0%; wavelength range: 190-400 nm).

[0029] Figure 5 is an ultraviolet-visible spectrum for dimethyl sulfoxide (only) (conditions: methanol solvent at a concentration of 1.0%; wavelength range: 190-820 nm).

[0030] Figure 5A is an ultraviolet spectrum (only) for dimethyl sulfoxide (only) (conditions: methanol solvent at a concentration of 1.0%; wavelength range: 190-400 nm).

[0031] Figure 6 is an ultraviolet-visible spectrum for menthyl glutarates (only) (conditions: methanol solvent at a concentration of 1.0%; wavelength range: 190-820 nm).

[0032] Figure 6A is an ultraviolet spectrum (only) for menthyl glutarates (only) (conditions: methanol solvent at a concentration of 1.0%; wavelength range: 190-400 nm).

[0033] Figure 7 is an ultraviolet-visible spectrum for WS 3® (only) (conditions: methanol solvent at a concentration of 1.0%; wavelength range: 190-820 nm).

[0034] Figure 7A is an ultraviolet spectrum (only) WS 3® (only) (conditions: methanol solvent at a concentration of 1.0%; wavelength range: 190-400 nm).

[0035] Figure 8A is an ultraviolet spectrum (only) for a 1:1 mixture of dimethyl sulfoxide:menthyl glutarates at a pH of 10 (conditions: aqueous solvent at pH of 10 at a concentration of 1.0%; wavelength range: 190-400 nm).

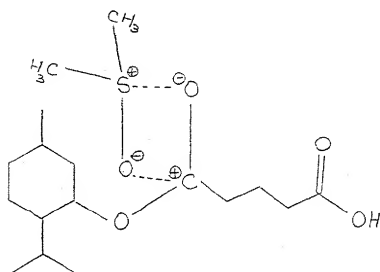
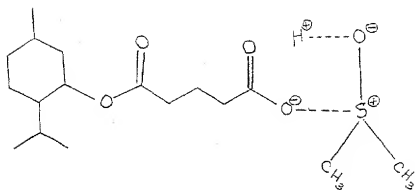
[0036] Figure 8B is an ultraviolet spectrum (only) for dimethyl sulfoxide (only) at a pH of 10 (conditions: aqueous solvent at a pH of 10 at a concentration of 1.0%; wavelength range: 190-300 nm).

[0037] Figure 8C is an ultraviolet spectrum (only) for a menthyl glutarates (only) at a pH of 10 (conditions: aqueous solvent at a pH of 10 at a concentration of 1.0%; wavelength range: 180-400 nm).

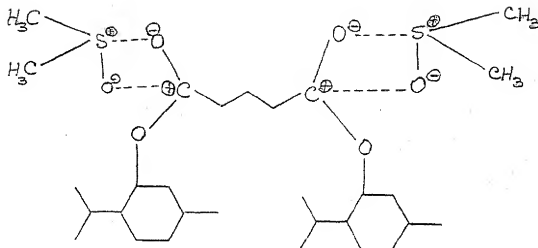
#### DETAILED DESCRIPTION OF THE DRAWINGS

[0038] Referring to Figure 1, the Y axis is for absorbents and the X axis is for wavelength. The Y axis is indicated by reference numeral 14 and the X axis is indicated by reference numeral 12.

[0039] Figure 1A is an enlargement of section "A" of Figure 1. The peak indicated by reference numeral 10 is the peak for the absorbents in the ultraviolet region of the 1:1 mixture of dimethyl sulfoxide:menthyl glutarates. Complexes formed as a result of the interaction of the dimethyl sulfoxide with menthyl glutarates have the following structures:

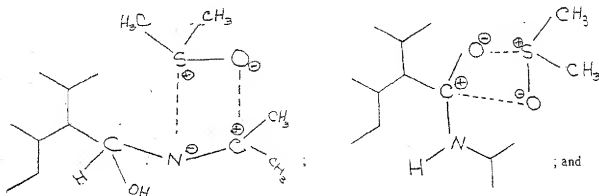


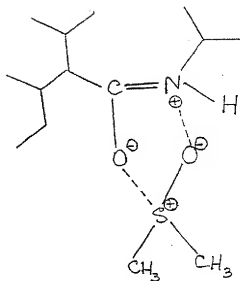
40 and



[0040] In Figures 2 and 2A (with Figure 2A being an enlargement of section "A" of Figure 2), the peak indicated by reference numeral 20 is the peak for the ultraviolet absorptivity of the 10:1 dimethyl sulfoxide menthyl glutarates mixture.

[0041] In Figures 3 and 3A (with Figure 3A being an enlargement of section "A" of Figure 3), the peak indicated by reference numeral 30 is the peak for the 1:1 mixture of dimethyl sulfoxide:WS 30. The complexes formed as a result of the interaction of dimethyl sulfoxide with WS 30 are as follows:





[0042] In Figures 4 and 4A, the peak indicated by reference numeral 40 is the peak for the ultraviolet absorptivity of the resulting material produced by admixing dimethyl sulfoxide with WS 30 in a weight ratio of 10:1. Figure 4A is an enlargement of section "A" of Figure 4.

[0043] In Figures 5 and 5A, the peak indicated by reference numeral 50 is the peak for the ultraviolet absorptivity of dimethyl sulfoxide alone. Figure 5A is an enlargement of section "A" of Figure 5.

[0044] In Figures 6 and 6A, the peak indicated by reference numeral 60 is the peak for the ultraviolet absorptivity of menthyl glutarates. Figure 6A is an enlargement of section "A" of Figure 6.

[0045] In Figures 7 and 7A, the peak indicated by reference numeral 70 is the peak for the ultraviolet absorptivity of WS 30 having the structure:

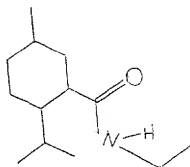
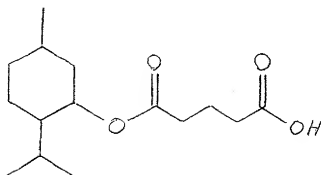


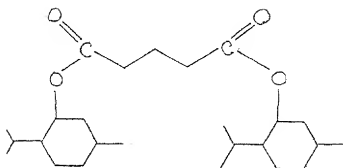
Figure 7A is an enlargement of section "A" of Figure 7.

[0046] In Figure 8A, the peak indicated by reference numeral 80 is the peak for the ultraviolet absorbants of the mixture of dimethyl sulfoxide and menthyl glutarates at a pH of 10 in the aqueous phase. In Figure 8B, the peak indicated by reference numeral 82 is the peak for the ultraviolet absorptivity at a pH of 10 of dimethyl sulfoxide alone. In Figure 8C, the peak indicated by reference numeral 84 is the peak for the ultraviolet absorptivity for menthyl glutarates at a pH of 10, alone.

[0047] In the foregoing descriptions of the drawings, when using the term "menthyl glutarates" it is to be understood that "menthyl glutarates" is a 70:30 mixture monomethyl glutarate having the structure:



15 and dimethyl glutarate having the structure:



30 [0048] The following examples are given to illustrate embodiments of the invention as it is preferred to practice it. It will be understood that these examples are illustrative, and the invention is not to be considered as restricted thereto, except as indicated in the appended claims.

35 **EXAMPLE I**

**ORAL HYGIENE FLAVOR FORMULATION**

40 [0049] The following basic oral hygiene flavor formulation is prepared:

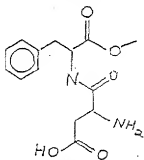
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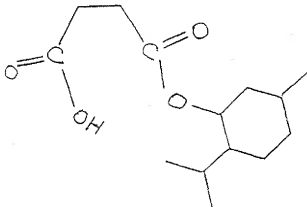
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Ingredients	Parts by Weight
Peppermint oil	89.0
Spearmint oil	2.0
Clove oil	1.0
Anethol	2.0
Cardamom oil	0.1
Wintergreen oil	5.0
Cinnamic aldehyde	0.9
Aspartame having the structure:	0.05



[0050] The basic oral hygiene flavor formulation is now divided into two parts. To the first part, a 1:50 mixture of dimethyl sulfoxide:menthyl succinate having the structure:

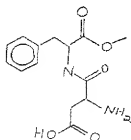


is added at the rate of 10%. To the second part, nothing is added. The flavor with the addition of the dimethyl sulfoxide:menthyl succinate mixture gives rise to a fresher, sweet, licorice, anise oil, spicy aroma and taste characteristics with aesthetically pleasing "cooling" nuances. The peppermint characteristics also appear to be enhanced. The flavor without the dimethyl sulfoxide:menthyl succinate mixture has an unpleasant aftertaste, which is not present in the mixture containing the dimethyl sulfoxide:menthyl succinate mixture. Accordingly, the dimethyl sulfoxide:menthyl succinate-containing composition is preferred by a five member bench panel.

## EXAMPLE II

### LICORICE CHEWING STICK

[0051] A flexible licorice stick is prepared in a standard manner. Prior to hardening at the level of 0.05 ppm, aspartame having the structure:



is added to the molten mixture. Also prior to hardening at the level of 6 ppb, a mixture of 2 parts dimethyl sulfoxide:20 parts menthyl lactate is added to the molten mixture. The molten mixture is molded into licorice sticks and hardened for marketing. Each of the licorice sticks has a pleasant, powerful, natural-like licorice anisic, China star anise oil flavor with intense and substantive "cooling" nuances. None of the licorice sticks have a bitter aftertaste. In the absence of the use of the composition which is a mixture of dimethyl sulfoxide and menthyl lactate, each of the licorice sticks, on consumption, does not have any "cooling" nuances imparted in the oral cavity and has a bitter aftertaste. Furthermore, the natural sweetness of each of the licorice sticks is enhanced as a result of the use of the mixture of dimethyl sulfoxide and menthyl lactate.

[0052] Preferably, when the dimethyl sulfoxide is admixed with the second sensory perception-affecting compound in order to form the compositions of our invention, the temperature of mixing is between about 15°C up to about 30°C at a pressure of from about 0.5 atmospheres up to about 2 atmospheres.

#### Claims

1. A composition comprising (i) dimethyl sulfoxide and (ii) at least one second compound selected from the group consisting of:

- (a) a compound containing at least one menthyl moiety;
- (b) a compound containing at least one vanillyl moiety; and
- (c) a compound containing at least one carboxamide moiety

wherein the weight ratio of second compound: dimethyl sulfoxide, is in the range of from about 1,000:1 down to about 3:10 and food grade acceptable salts thereof.

2. An oral sensory perception-imparting beverage comprising an aqueous beverage base and admixed therewith in a sensory perception-imparting quantity and concentration, the composition of Claim 1.
3. An oral sensory perception-imparting chewing gum comprising a chewing gum base and admixed therewith in an oral sensory perception-imparting quantity and concentration, the composition of Claim 1.
4. An oral sensory perception-imparting consumable article having intensified and substantive oral sensory perception-imparting properties, which is an ultimate product selected from the group consisting of beverages, toothpastes, throat lozenges, hard candies, mouthwashes, dental floss, chewing gums, edible films and chewable pharmaceutical products comprising:

- (i) an ultimate product base and intimately admixed therewith
- (ii) the composition of Claim 1

wherein the concentration of dimethyl sulfoxide based on the weight of ultimate product is from about 0.05 up to about 200 ppm, and the concentration of second compound is from about 2 up to about 10,000 ppm on a premixed basis.

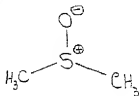
5. A complex of (i) dimethyl sulfoxide and (ii) at least one compound selected from the group consisting of:

- (a) menthyl moiety-containing compounds;

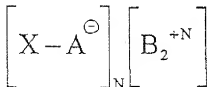
- (b) vanillyl moiety-containing compounds; and  
 (c) carboxamide moiety-containing compounds;

ingestible alkali metal and alkaline earth metal salts thereof, and ingestible alkaline earth metal polymers thereof

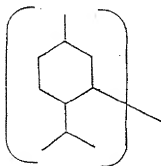
6. An oral sensory perception-imparting composition having intensified and substantive oral sensory perception properties consisting essentially of a product produced by the step of admixing dimethyl sulfoxide having the structure:



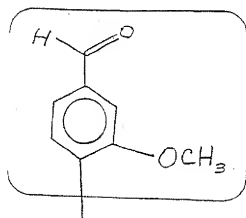
with at least one second compound having a formula selected from the group consisting of:  
 X-A-H; X-A-B<sub>1</sub>; and



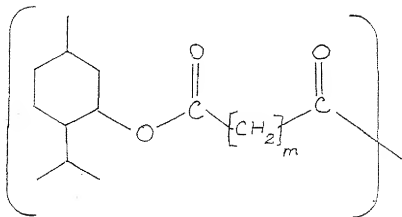
wherein in the weight ratio of second compound: dimethyl sulfoxide, is from 1,000:1 up to 3:10;  
 wherein the step of admixing is carried out at a temperature of from 15°C up to 30°C at a pressure of from about 0.5 up to about 2 atmospheres; and wherein X is a menthyl moiety having the structure:



a vanillyl moiety having the structure:

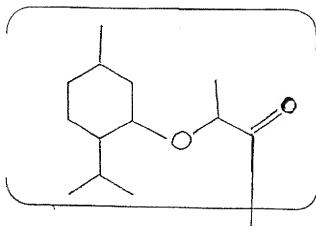


a menthoxy maleyl, glutaryl or succinyl moiety defined according to the structure:

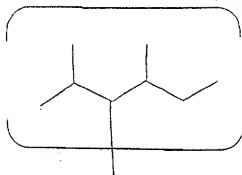


wherein m is an integer of from 1 up to 4;

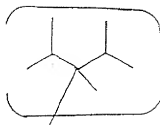
a menthoxy lactyl moiety having the structure:



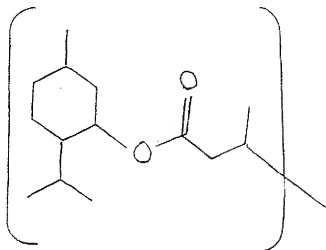
a 2,4-dimethyl-3-hexyl moiety having the structure:



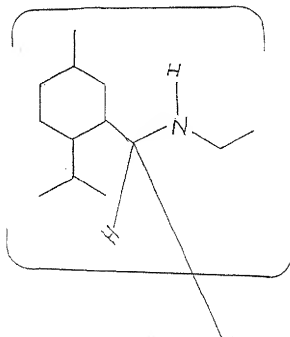
a 2,3,4-trimethyl-3-pentyl moiety having the structure:



a moiety having the structure:



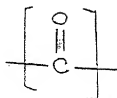
and a moiety having the structure:



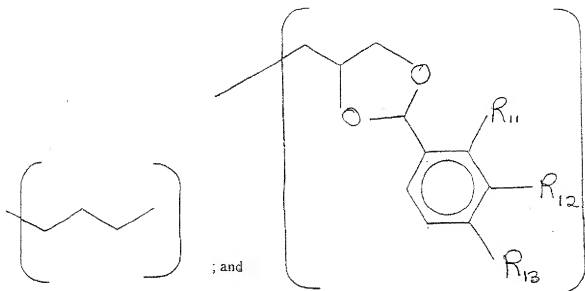
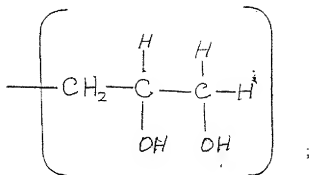
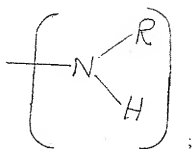
wherein A is a divalent ether oxygen moiety or alcohol oxygen moiety having the structure:



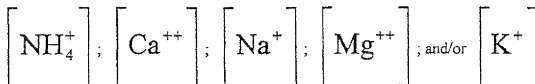
or a divalent carbonyl moiety having the structure:



; wherein B<sub>1</sub> is a moiety selected from the group consisting of:



wherein  $R_{11}$ ,  $R_{12}$  and  $R_{13}$  are each the same or different hydrogen or  $C_1$ - $C_3$  lower alkyl; wherein the concentration of dimethyl sulfoxide based on the weight of ultimate product is from about 0.05 up to about 200 ppm and the concentration of second compound based on the weight of ultimate product is from about 2 up to about 10,000 ppm on a premixed basis; and wherein  $B_2$  is a cation selected from the group consisting of:



and N is an integer of 1 or 2.

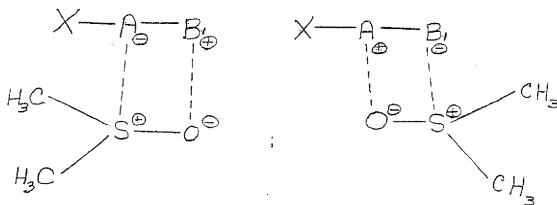
7. An oral sensory perception-imparting consumable article having intensified and substantive oral sensory perception-imparting properties, which is an ultimate product selected from the group consisting of beverages, tooth-pastes, throat lozenges, hard candies, mouthwashes, dental floss, chewing gums, edible films and chewable pharmaceutical products comprising:

(i) an ultimate product base and intimately admixed therewith

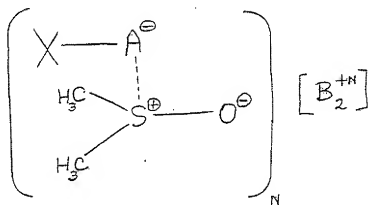
(ii) the composition of Claim 6

wherein the concentration of dimethyl sulfoxide based on the weight of ultimate product is from about 0.05 up to about 200 ppm, and the concentration of second compound is from about 2 up to about 10,000 ppm on a premixed basis.

8. A complex having a structure selected from the group consisting of:

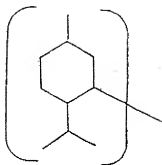


and

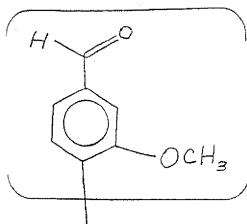


wherein X is a menthyl moiety having the structure:

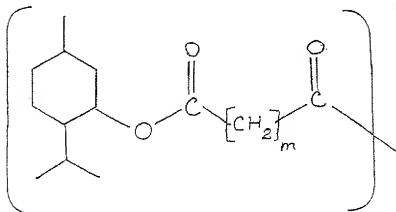




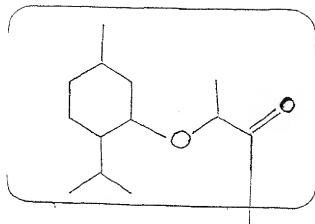
a vanillyl moiety having the structure:



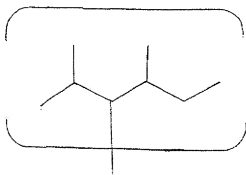
a menthoxy maleyl, glutaryl or succinyl moiety defined according to the structure:



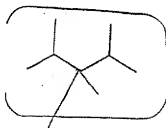
wherein m is an integer of from 1 up to 4;  
a menthoxy lactyl moiety having the structure:



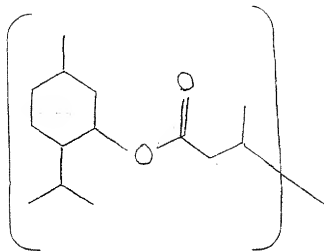
a 2,4-dimethyl-3-hexyl moiety having the structure:



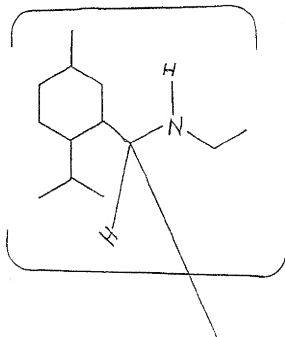
a 2,3,4-trimethyl-3-pentyl moiety having the structure:



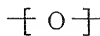
a moiety having the structure:



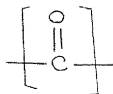
and a moiety having the structure:



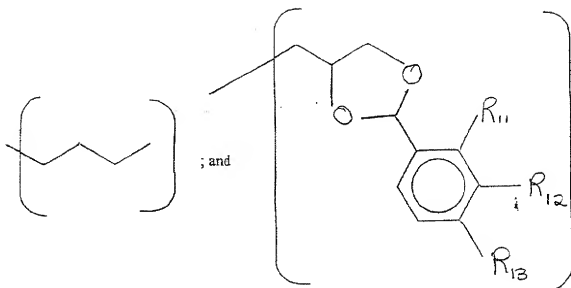
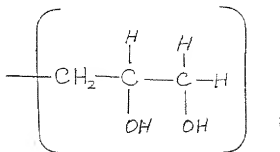
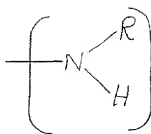
wherein A is a divalent ether moiety having the structure:



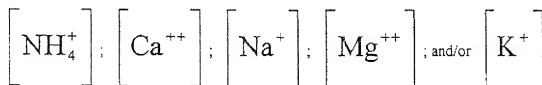
or a divalent carbonyl moiety having the structure:



; wherein  $B_1$  is a moiety selected from the group consisting of:



wherein  $R_{11}$ ,  $R_{12}$  and  $R_{13}$  are each the same or different hydrogen or  $C_1$ - $C_3$  lower alkyl; wherein the concentration of dimethyl sulfoxide based on the weight of ultimate product is from about 0.05 up to about 200 ppm and the concentration of second compound based on the weight of ultimate product is from about 2 up to about 10,000 ppm on a premixed basis; and ; and wherein  $B_2$  is a cation selected from the group consisting of:



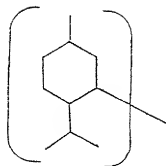
and N is an integer of 1 or 2

9. A composition comprising

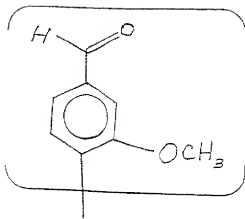
- (i) dimethyl sulfoxide; and
- (ii) at least one second compound selected from:
  - (a) a compound containing at least one menthyl moiety;
  - (b) a compound containing at least one vanillyl moiety;
  - (c) a compound containing at least one carboxamide moiety; or
  - (d) a compound having a formula selected from:  $X-A-H$ ;  $X-A-B_1$ ; and



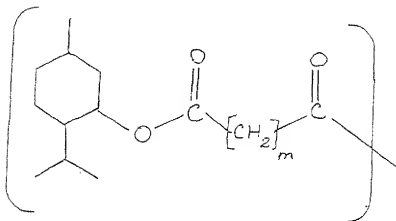
wherein X is a menthyl moiety having the structure;



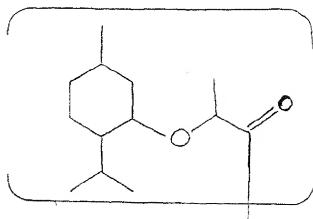
a vanillyl moiety having the structure:



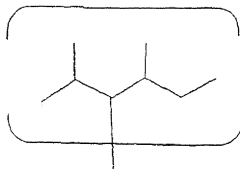
a menthoxy maleyl, glutaryl or succinyl moiety defined according to the structure:



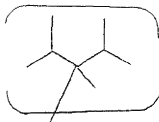
wherein  $m$  is an integer of from 1 up to 4;  
a menthoxy lactyl moiety having the structure:



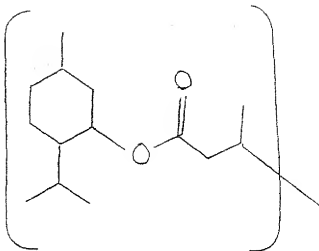
a 2,4-dimethyl-3-hexyl moiety having the structure:



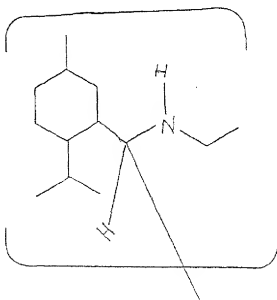
a 2,3,4-trimethyl-3-pentyl moiety having the structure:



a moiety having the structure:



and a moiety having the structure:



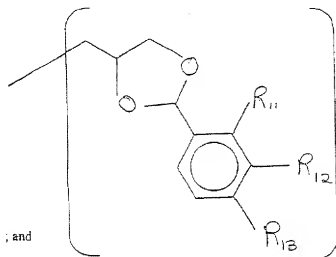
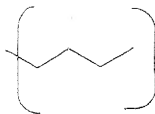
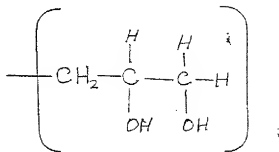
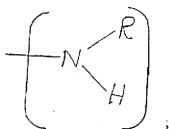
wherein A is a divalent ether oxygen moiety or alcohol oxygen moiety having the structure:



or a divalent carbonyl moiety having the structure:

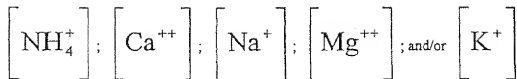


; wherein  $B_1$  is a moiety selected from the group consisting of:



wherein  $R_{11}$ ,  $R_{12}$  and  $R_{13}$  are each the same or different hydrogen or  $C_1$ - $C_3$  lower alkyl;  
and wherein  $B_2$  is a cation selected from the group consisting of:





and N is an integer of 1 or 2;  
and salts thereof.

10. A method of making a composition according to Claim 9 comprising the step of admixing (i) dimethyl sulfoxide with at least one compound as defined in part (ii) of Claim 9.
11. A consumable article containing the composition of Claim 9.
12. A consumable article according to Claim 11 wherein the consumable article is a beverage, toothpaste, throat lozenge, hard candy, mouthwash, dental floss, chewing gum, edible film, or a chewable pharmaceutical product.

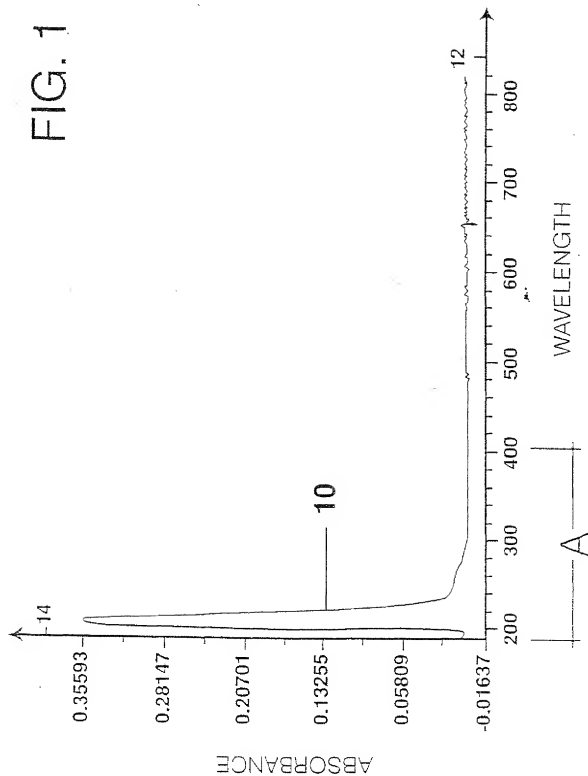


FIG. 1-A

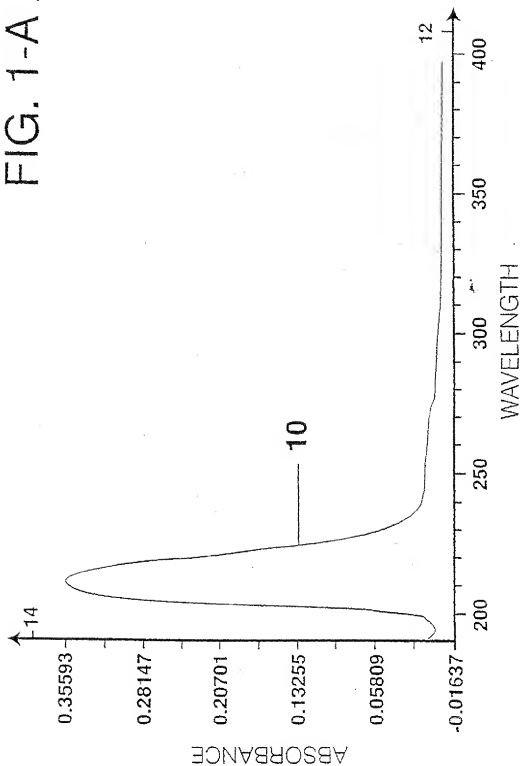


FIG. 2

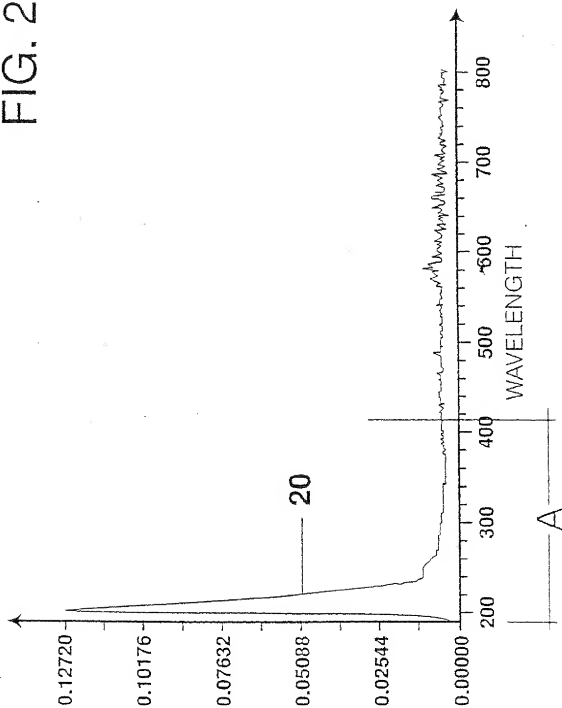


FIG. 2-A

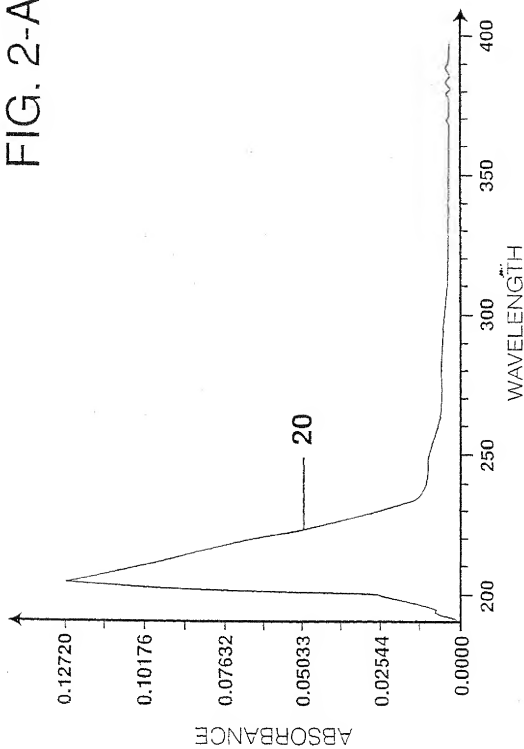


FIG. 3

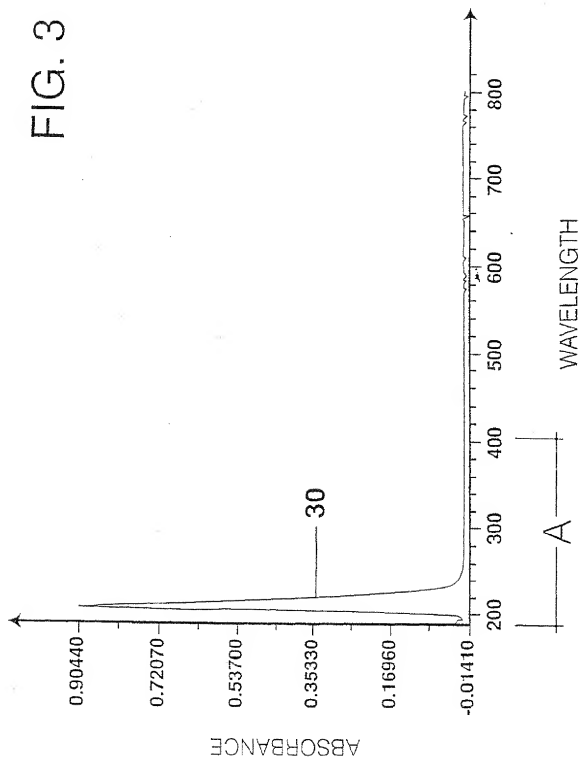


FIG. 3-A

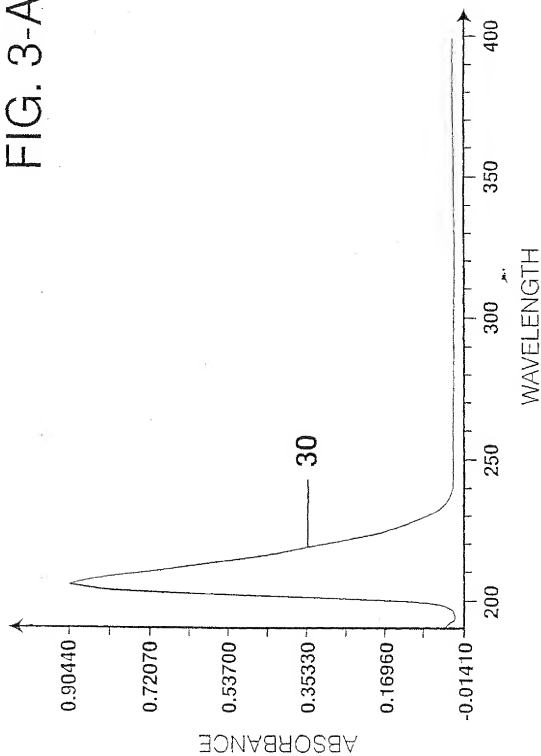


FIG. 4

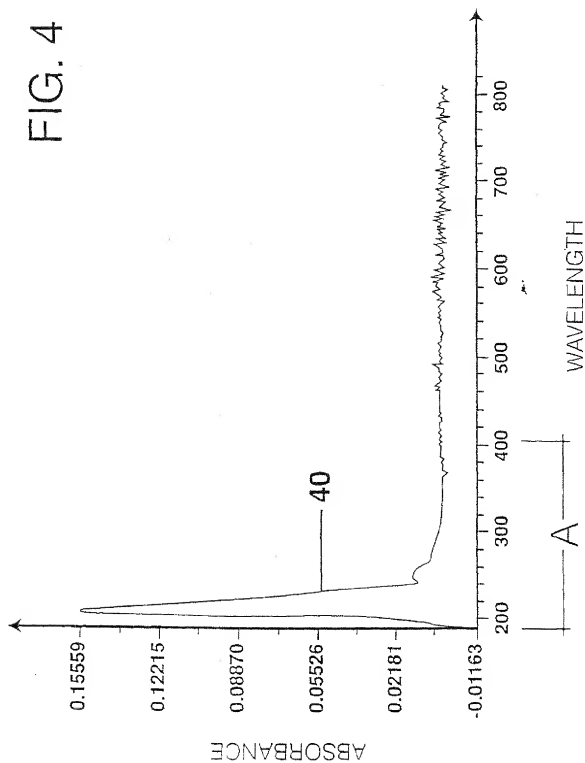




FIG. 4-A

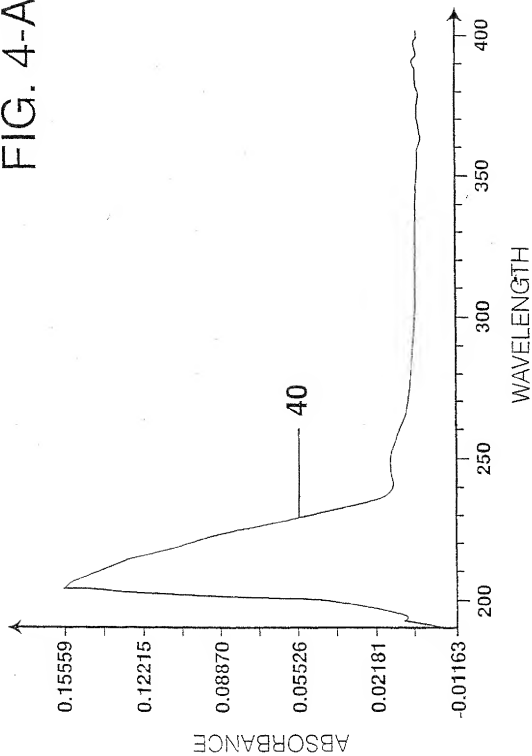


FIG. 5

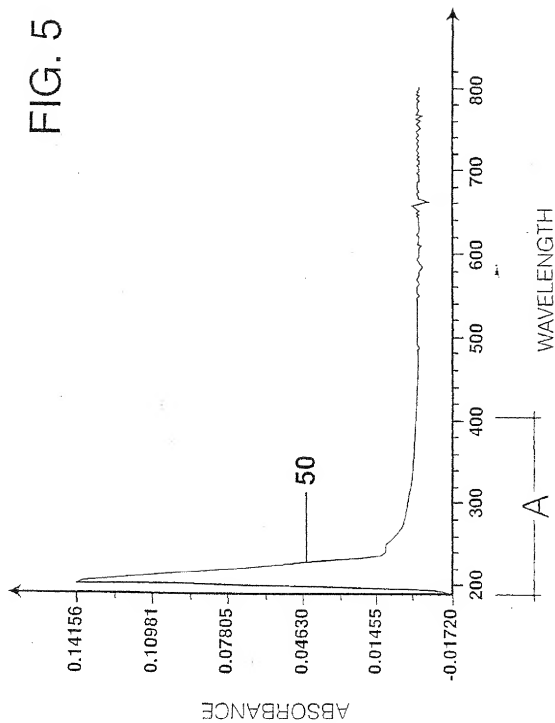


FIG. 5-A

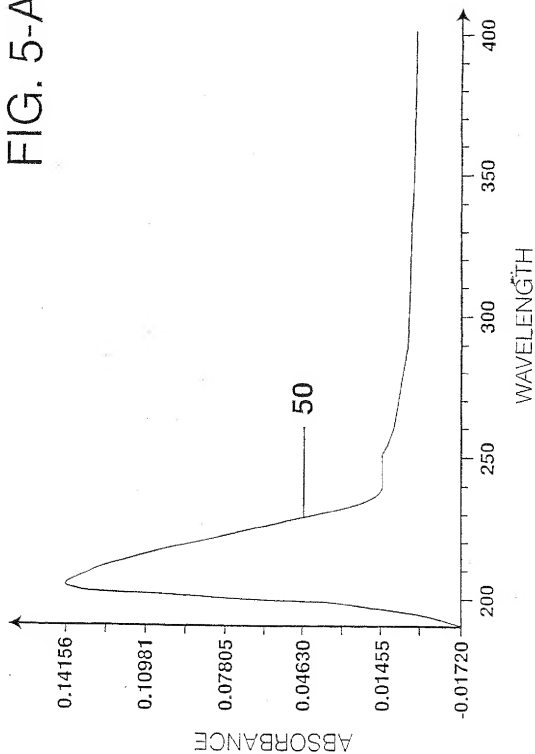


FIG. 6

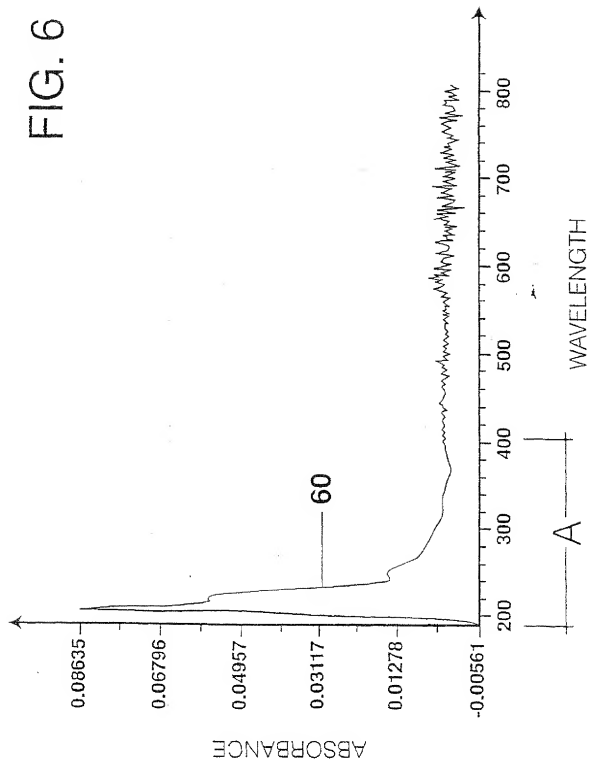
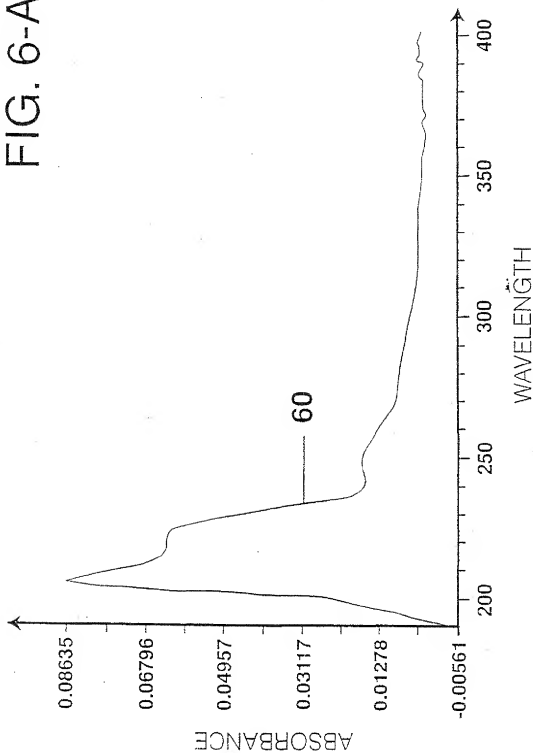


FIG. 6-A



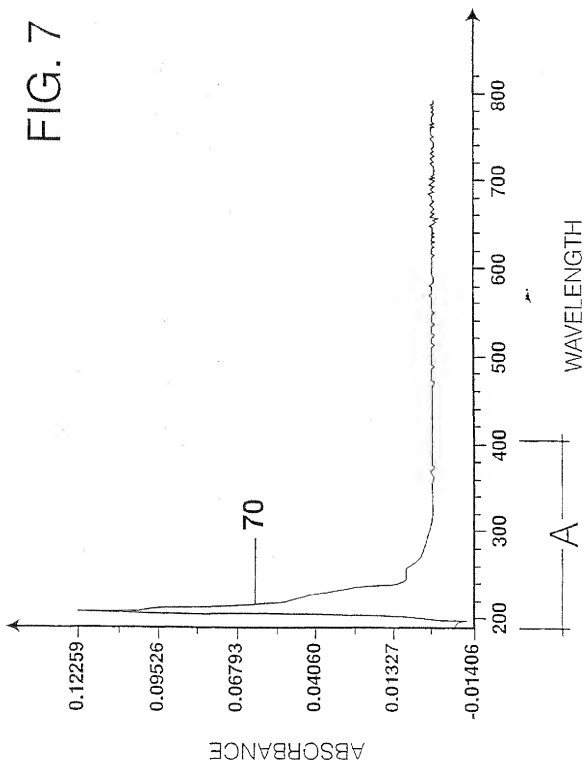


FIG. 7-A

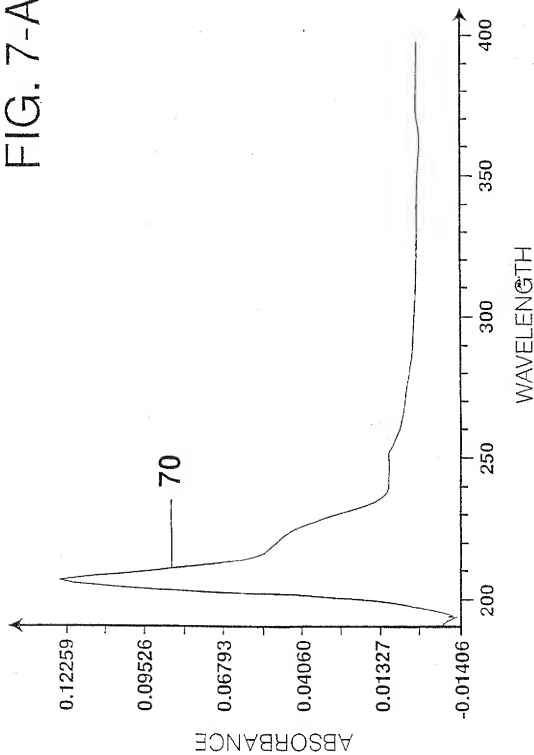


FIG. 8-A

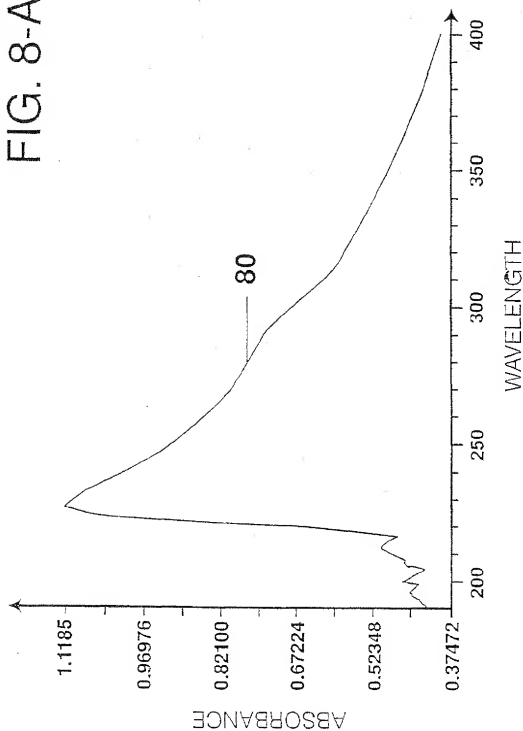




FIG. 8-B

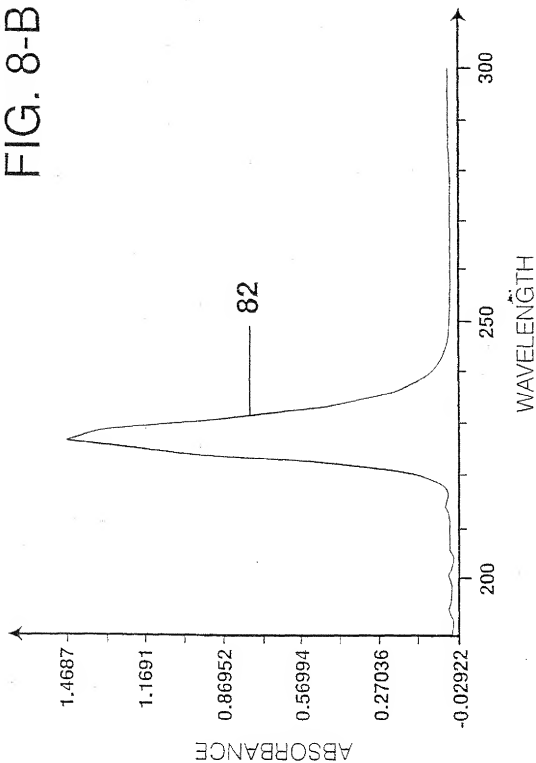
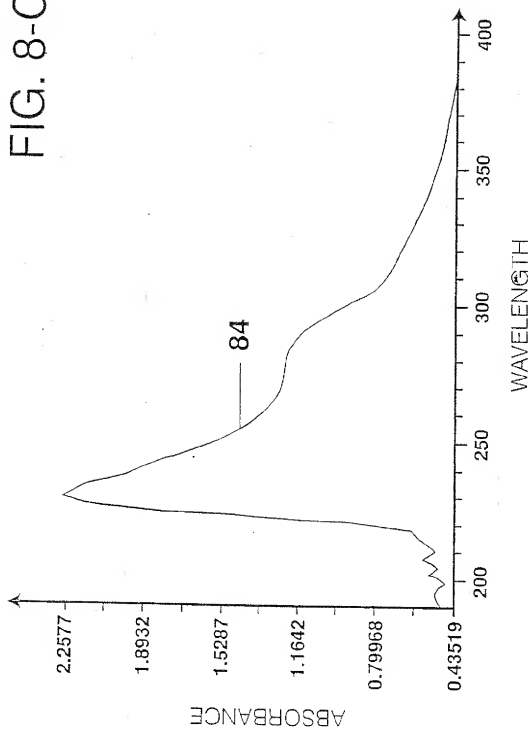


FIG. 8-C



(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

**EP 1 205 116 A3**

(12)

**EUROPEAN PATENT APPLICATION**

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12.11.2003 Bulletin 2003/46

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A23L 2/26**

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(30) Priority: **09.11.2000 US 710452**

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(54) **Oral sensory perception-affecting compositions containing dimethyl sulfoxide**

(57) Described are oral sensory perception-affecting compositions containing dimethyl sulfoxide, complexes thereof and salts thereof, specifically:

- (i) dimethyl sulfoxide; and
- (ii) a second compound or group of compounds:
  - (a) containing at least one menthyl moiety; and/or
  - (b) containing at least one vanillyl moiety; and/or
  - (c) containing at least one carboxamide moiety

thyl sulfoxide, is in the range of from about 1,000:1 down to about 3:10 and food grade acceptable salts thereof. Also described are oral sensory perception-affecting (e.g., "coolant")-impacting consumable articles (e.g., mouthwashes and the like) comprising a consumable article base and at least one of the aforementioned oral sensory perception-affecting compositions. Also described are complexes of (i) dimethyl sulfoxide and (ii) at least one of the aforementioned second compounds or group(s) of compounds.

when the weight ratio of "second compound(s)": dime-



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 01 30 8649

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Y	DATABASE WPI Section Ch, Week 199727 Derwent Publications Ltd., London, GB; Class B04, AN 1997-289806 XPO02254586 & CN 1 103 285 A (LI F), 7 June 1995 (1995-06-07)	1-12	A23L1/226 A61K7/16 A23L2/26
X	* abstract *	1,5,10	
Y	US 5 288 497 A (HAGUE BRIAN ET AL) 22 February 1994 (1994-02-22) * column 10, line 9 - column 11, line 12 * * column 16, line 50 - line 63; claims 1,182; examples 1,2 *	1-12	
Y	WO 99 30705 A (GARNER WILLIAM DARWIN ;GRIFFIN MARTIN J (US)) 24 June 1999 (1999-06-24) * claims 7-9 *	1-12	
Y,D	WO 93 23005 A (PROCTER & GAMBLE) 25 November 1993 (1993-11-25) * the whole document *	1-12	TECHNICAL FIELDS SEARCHED (Int.Cl.7)  A23L A61K
D,Y	WO 99 13734 A (WITKEWITZ DAVID L ;WOLF FRED R (US); HOOK JEFFREY S (US); MCGREW G) 25 March 1999 (1999-03-25) * abstract * * page 19, line 8 - line 12 *	1-12	
D,Y	US 5 009 893 A (CHERUKURI SUBRAMAN R ET AL) 23 April 1991 (1991-04-23) * abstract; table 1 *	1-12	
A	GB 1 432 354 A (WILKINSON SWORD LTD) 14 April 1976 (1976-04-14) * the whole document *	1-12	
-/-			
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		16 September 2003	Dauksch, H
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background P : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 01 30 8649

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL7)
A	US 4 353 896 A (LEVY MICHAEL A) 12 October 1982 (1982-10-12) * abstract; claim 1 *	1-12	
A	US 5 753 270 A (BEAUCHAMP PATRICK A ET AL) 19 May 1998 (1998-05-19) * column 4, line 18 - line 33 *	1-12	
A	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 02, 31 March 1995 (1995-03-31) & JP 06 321743 A (SANKYO CO LTD), 22 November 1994 (1994-11-22) * abstract *	1-12	
D,A	US 4 029 759 A (D AUDIFFRET YVES TOLLARD ET AL) 14 June 1977 (1977-06-14) * abstract *	1-12	
D,A	US 5 545 424 A (GREEN CARTER B ET AL) 13 August 1996 (1996-08-13) * abstract *	1-12	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. CL7)
Place of search		Date of completion of the search	Examiner
THE HAGUE		16 September 2003	Dauksch, H
CATEGORY OF CITED DOCUMENTS			
<p>X: particularly relevant if taken alone  Y: particularly relevant if combined with another document of the same category  A: technological background  O: non-written disclosure  P: intermediate document</p> <p>T: theory or principle underlying the invention  E: earlier patent document, but published on, or after the filing date  D: document cited in the application  L: document cited for other reasons  &amp;: member of the same patent family, corresponding document</p>			

ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

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